

**Kinetics of Pyromorphite Dissolution as Influenced by Aging**

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Beamline(s): X11A

**Introduction:** Stability of immobilized Pb as pyromorphite may significantly reduce the bioavailability of Pb in soil and aquatic environments. In this study, we examined the dissolution characteristics of aged pyromorphite using nitric acid at pH values of 2.0, 4.0, and 6.0. X-ray absorption fine structure (XAFS) spectroscopy and high-resolution thermogravimetric analysis (HRTGA) were employed to monitor chemical and physical alterations, however, due to the high stability of pyromorphite, little change was noted during dissolution.

**Methods and Materials:** Pyromorphite was created by mixing 0.25 M  $\text{PbCl}_2$  and 0.15 M  $\text{H}_3\text{PO}_4$  in 2 L HDPE bottles at a pH of 7.0 and under a  $\text{N}_2$  atmosphere. Aging times ranged from 1 hour to 1 year. The dissolution experiments included stirred-flow and batch methods using a combination of aging times and acid concentrations. The solid samples were collected at the end of the dissolution experiment and analyzed by XAFS and HRTGA.

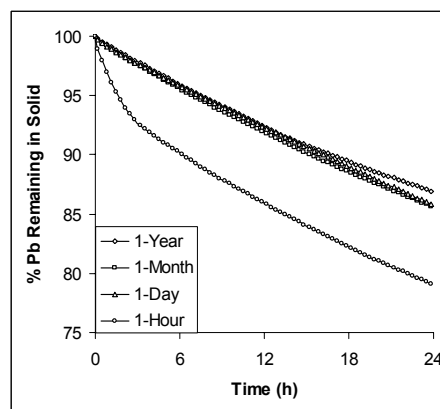
**Results:** Stirred-flow and batch dissolution studies determined that as pH of the dissolution agent decreased, the amount of dissolved Pb in solution increased. These studies (Figure 1) also observed little difference in the dissolution behavior of the 1-day and 1-year samples demonstrating a rapid aging process. Figure 2 shows the RSFs for 1-month aged pyromorphite after dissolution with nitric acid and fits to these data suggest Pb is octahedrally coordinated in the first shell with 6 oxygen atoms (3 @ 2.62Å and 3 @ 2.85Å). The second shell data comprised of three additional oxygen atoms located at approximately 3.01Å as well as three phosphorus atoms at 3.43Å. These data are in line with natural pyromorphite and did not change relative to the untreated 1-month sample. HRTGA, also, did not indicate differences in the dissolution of the 1-month sample. Figure 3 shows the derivatives of weight loss versus temperature for the dissolution samples. The HRTGA curves for the dissolution samples are unchanged in comparison to the untreated 1-month aged sample.

**Conclusions:** Pyromorphite formation is kinetically rapid and thermodynamically stable; ideal conditions for an in-situ, immobilization remediation technique [1-3]. XAFS identified no changes with regard to dissolution of the crystal structure of pyromorphite based on coordination environment and interatomic bond distances. HRTGA investigations noted no changes in the thermostability of the aged pyromorphites. Conversion of soil-Pb to pyromorphite may greatly reduce the bioavailability of Pb in contaminated soils.

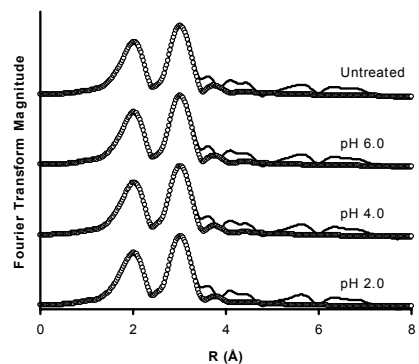
**Acknowledgments:** The research results presented herein do not, necessarily, reflect Agency policy. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

**References:**

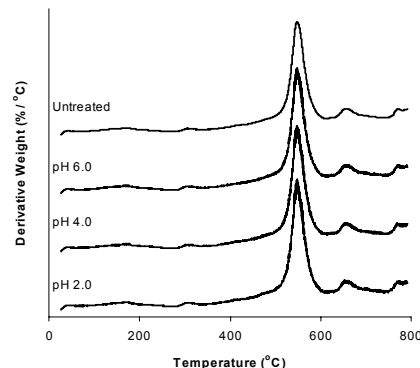
1. Zhang, P.C. and J.A. Ryan, *Formation of pyromorphite in anglesite hydroxyapatite suspensions under varying pH conditions*. Environ. Sci. Technol. 1998. **32**(21): p. 3318-3324.
2. Zhang, P.C. and J.A. Ryan, *Transformation of Pb(II) from cerussite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH*. Environ. Sci. Technol. 1999. **33**(4): p. 625-630.
3. Zhang, P.C., J.A. Ryan, and J. Yang, *In vitro soil Pb solubility in the presence of hydroxyapatite*. Environ. Sci. Technol. 1998. **32**(18): p. 2763-2768.



**Figure 1.** Stirred-flow dissolution of aged pyromorphite with nitric acid (pH 2.0).



**Figure 2.** RSFs of 1-month aged pyromorphite dissolution.



**Figure 3.** HRTGA of 1-month aged pyromorphite dissolution.